

Size-Fractionation of Molybdenum Disulfide Nanoparticles

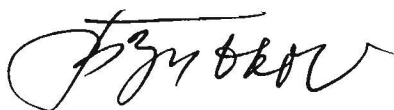
An Honors Thesis (HONRS 499)

by

Matthew Bailey

Thesis Advisor

Dr. Tykhon Zubkov

A handwritten signature in black ink, appearing to read 'Tykhon Zubkov', with a large, stylized initial 'T'.

**Ball State University
Muncie, Indiana**

April 2011

Expected Date of Graduation

May 2011

SpColl
Undergrad.
Thesis
LD
2489
.24
2011
.035

Abstract

Molybdenum disulfide is a narrow-band semiconductor that acquires promising photocatalytic properties when dispersed on the nanometer scale. This is due to the bandgap widening, which depends on the particle size. Many synthesis methods yield polydisperse nanoparticle samples. There is a need for size-fractionation of the MoS₂ nanoparticles to target the specific size-dependent properties. MoS₂ nanoparticles in this study were synthesized by decomposing Mo(CO)₆ in solutions in the presence of dissolved sulfur. The particles obtained were in the 5-40 nm size range. Size-fractionation with an ultracentrifuge was attempted in different ways. Sedimentation centrifugation in pure cyclohexane for three minutes with increasing speeds involved repeated harvesting of the sedimenting portions of MoS₂. Limited fractionation was achieved. For density gradient centrifugation, cyclohexane and bromoform were chosen to create a gradient because of the large difference in their densities. Centrifugation at 1000rpm for three minutes resulted in the particle distribution through the centrifuge tube. Harvested fractions were largely polydisperse with the particle size varying by a factor of 2-3 within each fraction. Some crude fractionation was achieved. Adding a viscous polymer, polystyrene, into the original gradient did not improve the separation drastically. Solid phase extraction with a silica media was attempted, but was unsuccessful because the particles would not elute from the column. Size exclusion chromatography was attempted using a poly (styrene-co-divinylbenzene) polymer media of two different grain sizes (200-400 and 300-800 μm) to fill the column. Several different parameters were used, but the method failed. The MoS₂ particles did not pass through the column. It is hypothesized that the pore sizes were too small to allow any of the particles to pass through. In summary, sedimentation centrifugation and simple density gradient with no additives yielded the best results.

Acknowledgements

I would like to thank Dr. Tykhon Zubkov for advising me throughout this project and for allowing me to work with him for the previous two years. Without his help I would not have been able to undertake such a difficult research project. His help has been instrumental in me completing this task, but it is also only a small fraction of the help and guidance I received during my four-year college career from many different faculty members. I would not be where I am today without their guidance.

Authors Statement

The purpose of this research project was to try and develop a method to separate a solution of molybdenum disulfide nanoparticles (1 meter=1,000,000,000 nanometers) based on their size. Molybdenum disulfide is an inorganic compound. There are a few different methods to make these nanoparticles, but the majority of them create a solution with a broad range of particle sizes. The method used to create the nanoparticles in this project yielded a solution of particles with a size range from 5-40 nanometers in diameter. On the nanometer scale these particles acquire important properties and in order to take advantage of those properties there must be a way to create a much smaller size range, even a specific size. That is the reason why developing a method of separating the particles based on size is important. There has not been a significant amount of research on this particular topic and there is none that has to do with the particles being worked with in this research project. Several different methods that are useful in separating other compounds were chosen. These methods were modified to fit the properties of our particles to see if they would work to separate them. In this thesis it is discussed how the nanoparticles were made and how the different separation methods were experimented with and the results of each.

Table of Contents

Chapter 1. Introduction.....	6
Chapter 2. Synthesis and Characterization of MoS ₂ Nanoparticles.....	7
2.1. Synthesis of MoS ₂ Nanoparticles in Decalin.....	7
2.2. Characterization of MoS ₂ Nanoparticles.....	10
Chapter 3. Sedimentation Centrifugation in Pure Cyclohexane.....	11
3.1. Ultracentrifugation.....	11
3.2. Imaging.....	12
Chapter 4. Density Gradient Centrifugation.....	14
4.1. Introduction to Density Gradient Centrifugation.....	14
4.2. Preliminary Studies.....	14
4.3. Cyclohexane and Bromoform Density Gradient Centrifugation.....	17
4.4. Density Gradient Centrifugation in Viscous Medium.....	20
Chapter 5. Solid Phase Extraction.....	23
Chapter 6. Size Exclusion Chromatography.....	24
Chapter 7. Conclusions.....	26
References.....	28

Chapter 1. Introduction

Molybdenum disulfide is a narrow-band semiconductor that forms atomically layered graphite-like sheets and is useful in the photocatalytic degradation of organics and the catalytic hydrosulfurization of petroleum.[1] Semiconductors have a band gap between their highest occupied molecular orbital and lowest unoccupied molecular orbital. If a photon with a great enough energy is absorbed, an electron will overcome this band gap and enter the conduction band. When this occurs, the electron can return to the valence band or alternatively the electron and the remaining hole in the valence band can travel to the surface to attach to a molecule causing oxidation or reduction.[2]

There are a few well known semiconductor photocatalysts, such as titania (TiO_2), but the problem with these is that they harvest sunlight inefficiently. This is because the band gap is greater than 3 eV.[3] Only blue, violet, and UV portions of the spectrum can be used. Because the band gap is so large, the main part of the solar spectrum is not harvested. Electrons excited by a photon often recombine with the hole in the valence band rather than moving to the surface to cause oxidation or reduction.[3] Due to these problems with titania-based photocatalysts there has been a shift in focus to narrow-band semiconductors, such as MoS_2 . Narrow-band semiconductors are capable of absorbing light throughout the visible spectrum because they have much smaller band gaps.[4]

Despite the ability to absorb light throughout the visible spectrum, narrow-band semiconductors have inherent problems. Electrons and holes photoexcited across a narrow band gap may not have enough redox potential to transfer onto outside molecules. This makes the material photocatalytically inactive.[3] This changes when these particles are dispersed on the

nanometer scale. When materials are small, their electronic and optical properties deviate substantially from those of bulk materials. As the dimensions of the particles reach a certain limit in the nanoscale, the band gap widens and becomes size dependent.[2] This means that when on the nanometer scale the band gaps of these nanomaterials can be tuned to make the material photocatalytically active. These characteristics demonstrate what an important role size plays in the properties of these particles. Many synthesis methods yield polydispersed nanoparticle samples. There is a need for size-fractionation of these polydispersed samples so the specific size-dependent properties can be targeted.

Chapter 2. Synthesis and Characterization of MoS₂ Nanoparticles

2.1. Synthesis of MoS₂ Nanoparticles in Decalin

The MoS₂ nanoparticles to be used in the different size-fractionation techniques were synthesized in a simple one-pot set-up that calls for the thermal decomposition of metal carbonyl in the presence of dissolved sulfur which is similar to a method described by Duphil *et al.*[5] Before the synthesis, all of the glassware for the apparatus was cleaned properly. Each piece was scrubbed visually clean and rinsed with acetone. They were then soaked in *aqua regia* for several hours to remove any traces that may have been left from previous use. Finally, they were rinsed with deionized water, dried with acetone, and then placed in an oven to make certain there was no trace of water before the synthesis began.

The synthesis apparatus was set up as shown in Figure 1. It consisted of a two-necked round bottom flask with a thermometer sleeve and a reflux condenser attached. All steps were carried out under argon pressure to prevent any reaction with oxygen. There were two valves: one placed in the free neck of the round bottom flask and one into the top of the reflux

condenser, which allowed the solvent to be degassed. This set-up meant that argon pressure could be maintained while transferring the solid material into the flask through one of the necks while argon flowed from the valve on the reflux condenser.



Figure 1. Apparatus used for the synthesis of MoS₂ nanoparticles.

500mL of decalin, a high-boiling non-coordinating solvent, was placed into the round bottom flask and the system was degassed for fifteen minutes by purging argon. The mole ratio of sulfur to metal carbonyl was kept at 2:1. 36.0 mg of sulfur was added to the decalin from a weigh boat and 1mL of decalin was used to wash the sulfur that stuck to the neck of the flask into the solution. All of the sulfur may not have made it into the solution due to static electricity on the weigh boat. The solution was warmed to reflux at 190-195°C and maintained there for ten minutes to dissolve the sulfur. After cooling to room temperature, 148.19 mg of the metal

carbonyl, Mo(CO)_6 , was added to the solution and heated to 90°C . The temperature was maintained at 90°C for four hours and then increased to $140\text{--}145^\circ\text{C}$ where it was maintained for three days. The heat was then turned off and the solution allowed to cool to room temperature under argon pressure. The solution was transferred to a clean bottle and the round bottom flask was washed with decalin to remove as much of the product as possible.

The synthesized particles were then isolated from their solvent. The mixture was agitated by sonication and then a portion was transferred to a plastic ultracentrifuge tube. This was placed in the ultracentrifuge for fifteen minutes at 12000 rotations per minute (rpm), and the clear, colorless supernatant was removed with a pipette. 50 mL of cyclohexane was added and the particles were re-dispersed by sonication. The solution was then centrifuged again at 12000 rpm for fifteen minutes and the supernatant removed again. This cycle was repeated a total of five times. The remaining portions of the original solution synthesized in decalin were cleaned in the same way. All cleaned portions were recombined into a round bottom flask and dried in a rotary evaporator. Once dry, the MoS_2 nanoparticles were re-dispersed in cyclohexane and placed in a clean bottle (Figure 2).



Figure 2. Synthesized MoS_2 nanoparticles dispersed in cyclohexane.

2.2. Characterization of MoS₂ Nanoparticles

To determine the size distribution of nanoparticles synthesized, images of the product were taken with a transmission electron microscope (TEM). The support grid for the TEM imaging had a carbon film supported by a copper grid. To prepare the sample, the product was agitated and a small sample was removed with a disposable glass pipette. Drops from the pipette were dried on the sample grid and then imaged. TEM images of the MoS₂ particles show nanoparticles ranging in size from 5-40 nm in diameter (Figure 3).

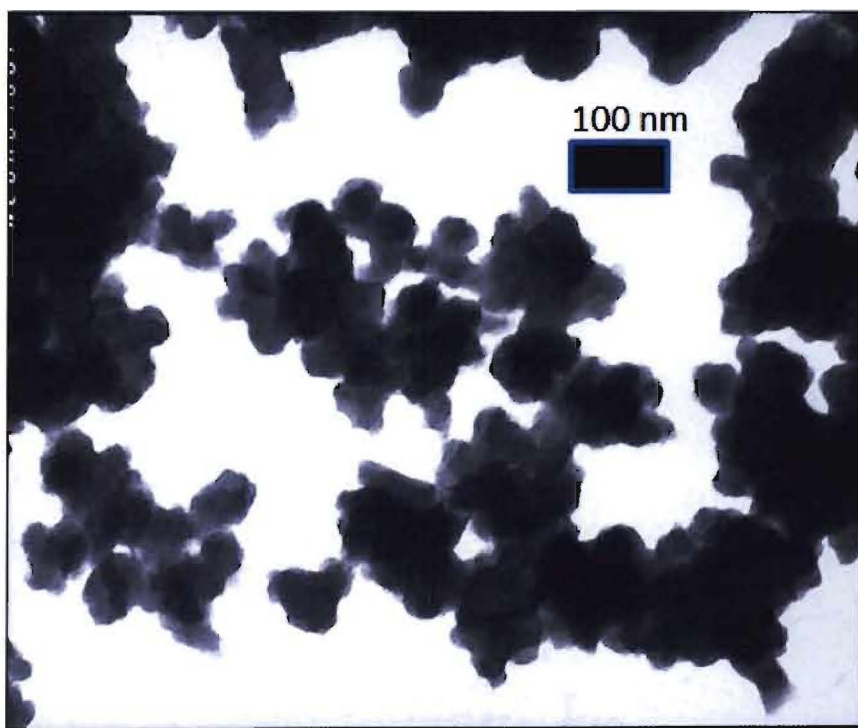


Figure 3. TEM image of synthesized MoS₂ nanoparticles

Lastly, UV-visible absorption spectra of the MoS₂ nanoparticles were taken. The sample was agitated and then placed in a quartz cuvette as spectra were recorded over time. The spectrum is shown in Figure 4. This spectrum illustrates the blue shift in optical absorption as the size of the particle decreases.

MoS₂ Nanoparticle Sedimentation Experiment

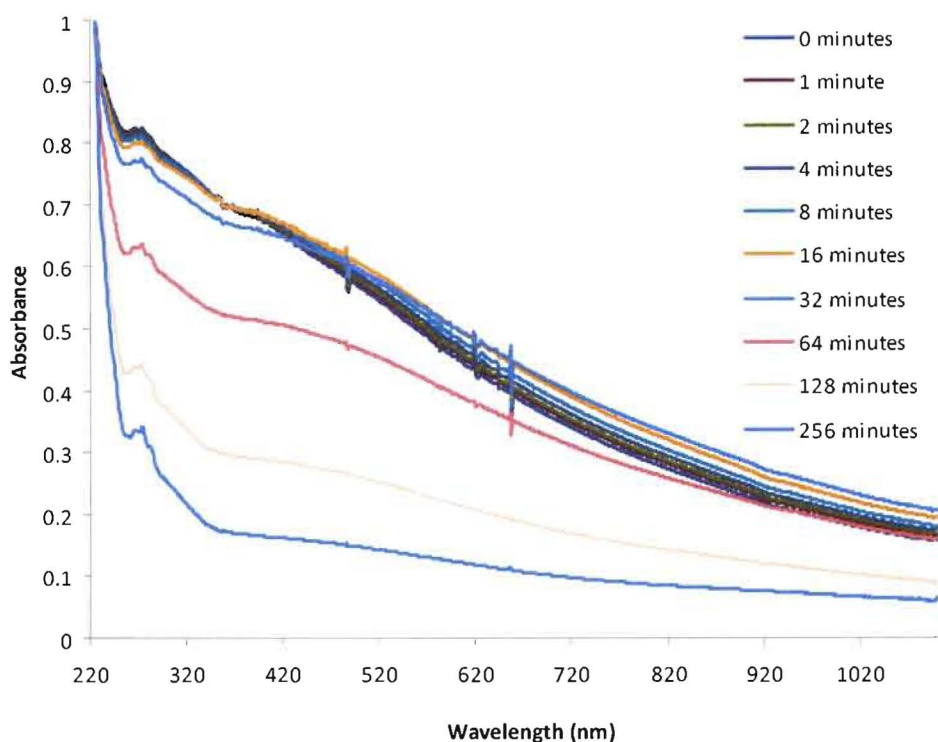


Figure 4. UV-Visible spectra of MoS₂ nanoparticles sedimenting over time.

Chapter 3. Sedimentation Centrifugation in Pure Cyclohexane

3.1. Ultracentrifugation

The first method of size-fractionation that was used was simple sedimentation ultracentrifugation. A polydisperse sample of the nanoparticles was placed in a plastic tube and centrifuged for three minutes at 1000 rpm. The supernatant, which was still dark because there were still particles present, was carefully pipetted off and placed in a clean centrifuge tube leaving the sedimented particles. The supernatant was then centrifuged for three minutes at 1500 rpm and the steps were repeated. This procedure was repeated until there were a total of eight fractions. The speed was increased by 500 rpm each time, but the time stayed consistent at three minutes. All of the samples were re-dispersed in cyclohexane and transferred to separate vials.

3.2. Imaging

To determine the size of particles and whether or not this method allowed for size-fractionation, TEM images of select fractions were taken. The same method of sample preparation described previously was used. Fractions 2, 4, and 6 (out of 8 total) were deposited and dried on the copper grid. Figures 5, 6, and 7 show the images.

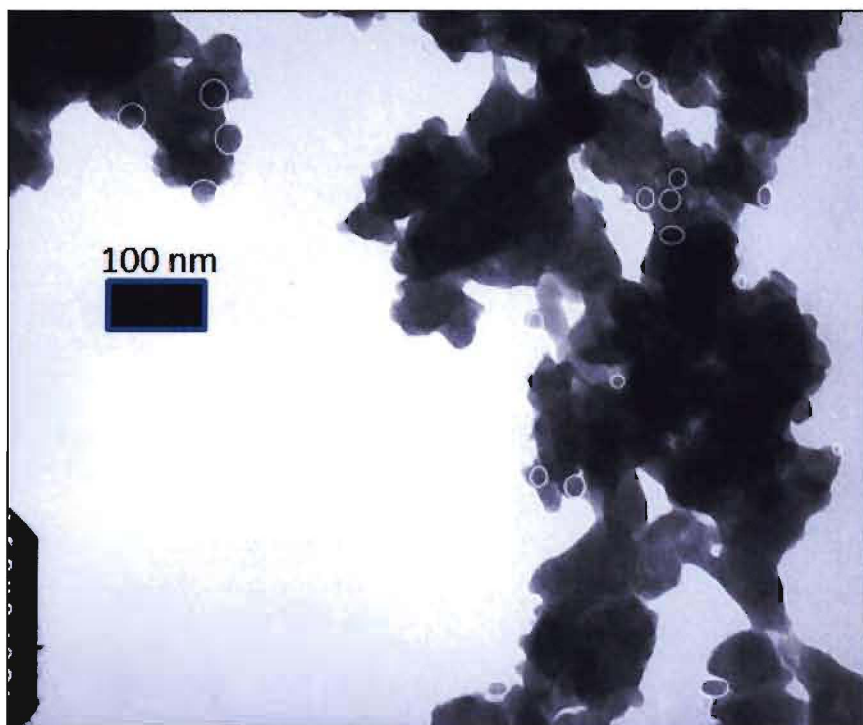


Figure 5. TEM image of fraction 2 from sedimentation centrifugation in pure cyclohexane.

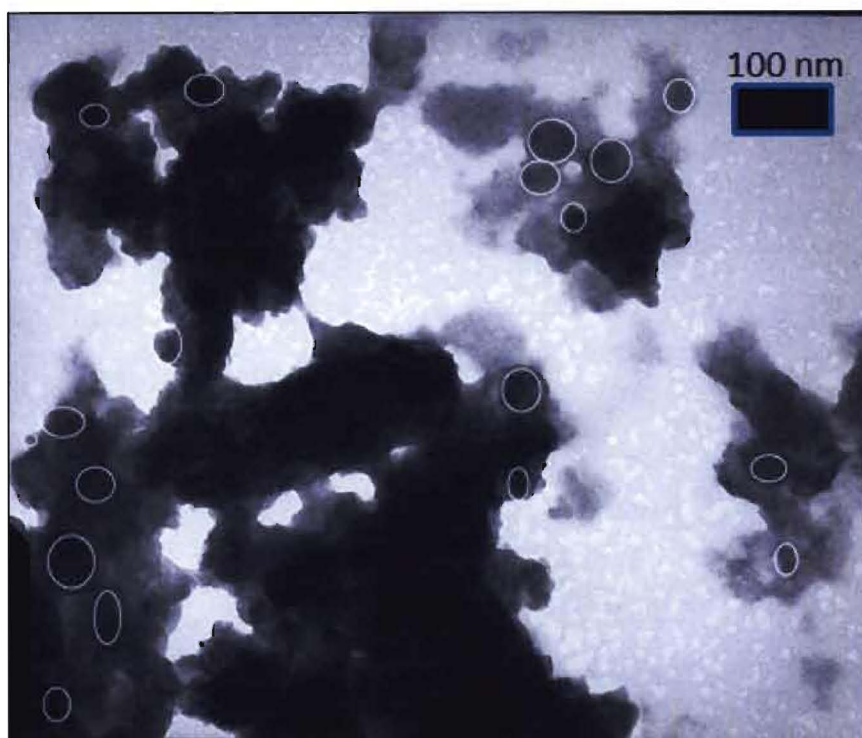


Figure 6. TEM image of fraction 4 from sedimentation centrifugation in pure cyclohexane.

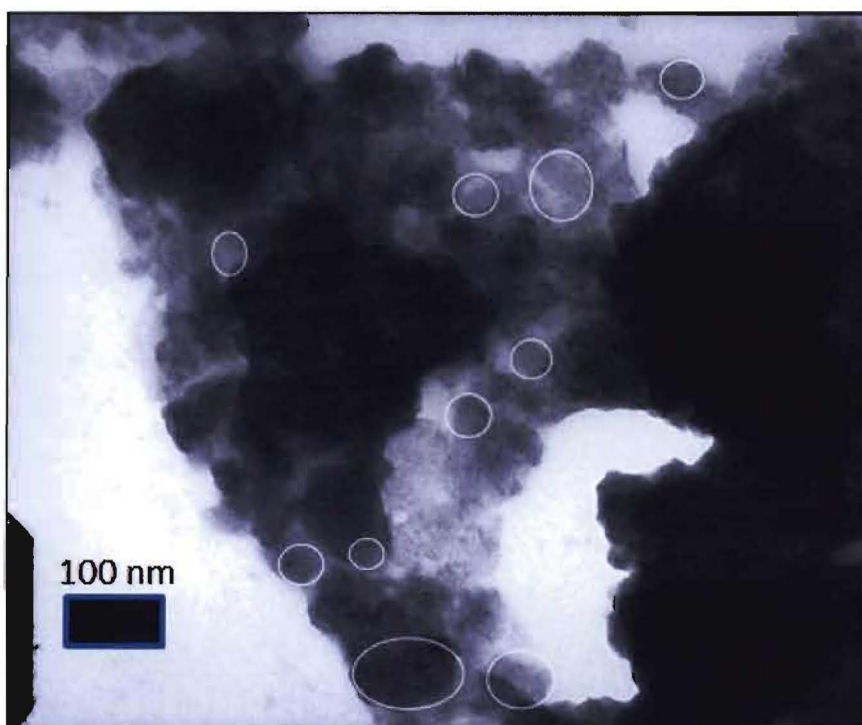


Figure 7. TEM image of fraction 6 from sedimentation centrifugation in pure cyclohexane.

From the differing sizes of particles between fractions that are shown by the TEM images it can be concluded that this method allows for moderate size-fractionation. This being said it is not a very efficient method because there is still a polydisperse distribution of sizes in each fraction. Therefore, it does not allow for a specific size to be separated.

Chapter 4. Density Gradient Centrifugation

4.1. Introduction to Density Gradient Centrifugation

The idea behind the application of density gradient centrifugation as a size-fractionation technique was inspired by the studies of Bai *et al.*[6,7] Bai was able to separate a colloid of gold nanoparticles dispersed in a nonhydroxylic solvent using ultracentrifugation in an organic density gradient. The density gradient was made up of the non-polar solvents cyclohexane and tetrachloromethane.[6] Until this study most ultracentrifugation separation work focused on aqueous density gradients and there have been few attempts to separate nanoparticles that are non-polar and dispersed in a non-polar organic solvent. The density gradient method is ideal because it is nondestructive and the results are measurable. MoS₂ nanoparticles are extremely hydrophobic and would not work in an aqueous density gradient. That is why the method described above could work well for them.

4.2. Preliminary Studies

Cyclohexane (density 0.779 g/mL) and chloroform (density 1.492 g/mL) were used as solvents. A density gradient was prepared by placing 20 mL of cyclohexane in an ultracentrifuge tube and pipetting 20 mL of chloroform underneath using a thin Pasteur pipet. The tube was tilted to a 45° angle and back 50 times to attempt to make a smooth gradient by slow mixing. Then 3 mL of the previously synthesized MoS₂ nanoparticles were carefully pipetted on top and

the solution was centrifuged for two minutes at 1000 rpm. When examined after centrifugation, the formation of rings of particles in different layers down the inside of the centrifuge tube was visible (Figure 8). This is most likely due to the unsuccessful creation of a smooth gradient and is not useful to us.

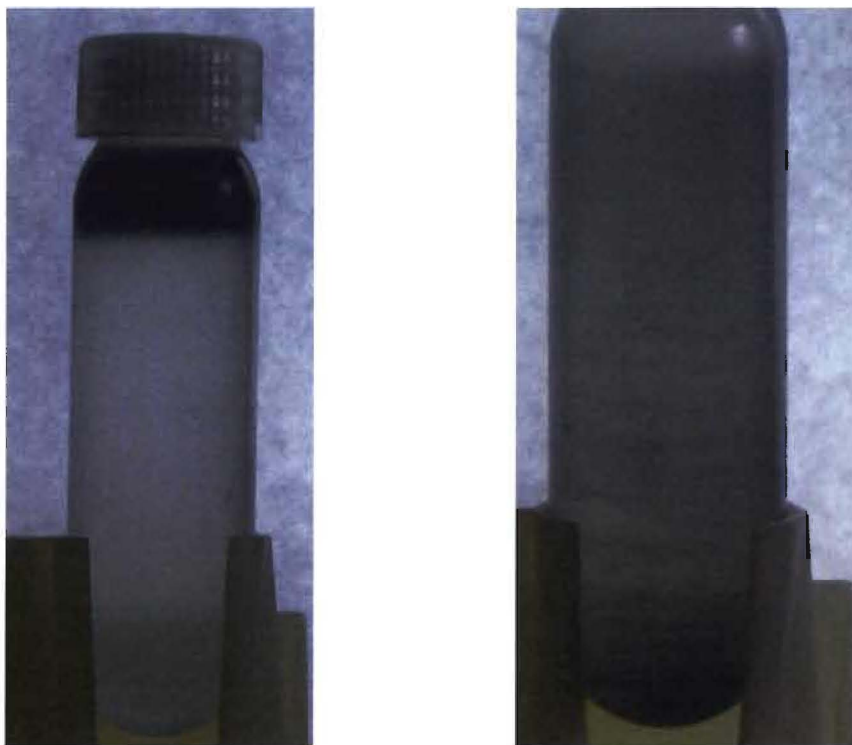


Figure 8. Ultracentrifuge tubes before centrifugation (left) and after (right) that shows the formation of rings of particles.

To confirm this, a solution of chloroform was made with methylene blue dissolved in it and the same gradient was created. When the fractions were harvested they were analyzed with a UV-Visible Spectrometer. By having methylene blue dissolved in the solution it could be determined if a smooth gradient was created by analyzing the absorbance spectrum and seeing if the absorbance due to methylene blue increased proportionally from fraction to fraction. Figure 9

shows the results. As suspected a smooth gradient was not created which would not allow for the particles to separate properly.

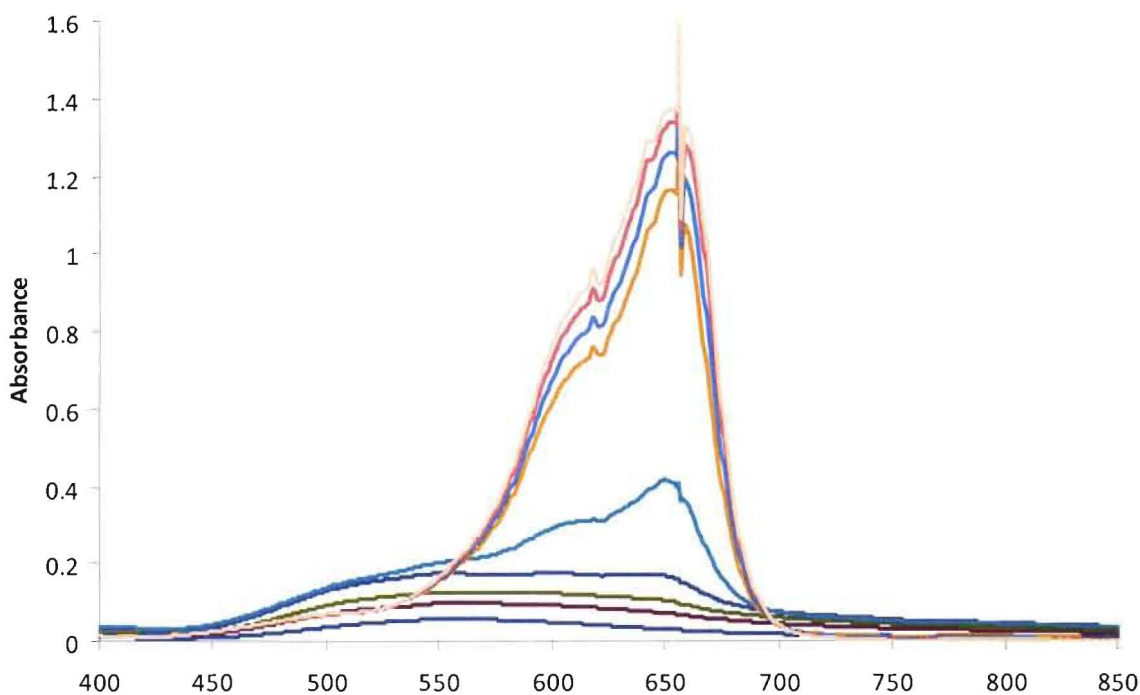


Figure 9. Levels of methylene blue along the tube are evident from the UV-visible spectrum of the density gradient created.

To solve this problem several different methods were attempted using the methylene blue solution. The same solution of chloroform with methylene blue dissolved in it was used. After each attempt of creating a smooth gradient, a certain number of fractions were harvested and analyzed on the UV-Visible Spectrometer. However, there was only one that was efficient, reproducible, and gave us a smooth gradient.

For this method, a 10-step gradient was created inside the centrifuge tube by making ten solutions with varying concentrations and placing 4 mL of each on top of each other. On the bottom was a 10%vol solution of cyclohexane, the next one was 20% cyclohexane, and so on

until a 100% solution of cyclohexane was on the top. The tube was then placed on its side for twenty minutes to allow the layers to begin to diffuse. It was then centrifuged for two minutes at 1000 rpm and nine fractions were obtained. Each was analyzed using the UV-Visible Spectrometer. Figure 10 shows that a smooth gradient of solutions is created. This optimal gradient preparation was then used for further studies using a cyclohexane and bromoform (density 2.89 g/mL) gradient.

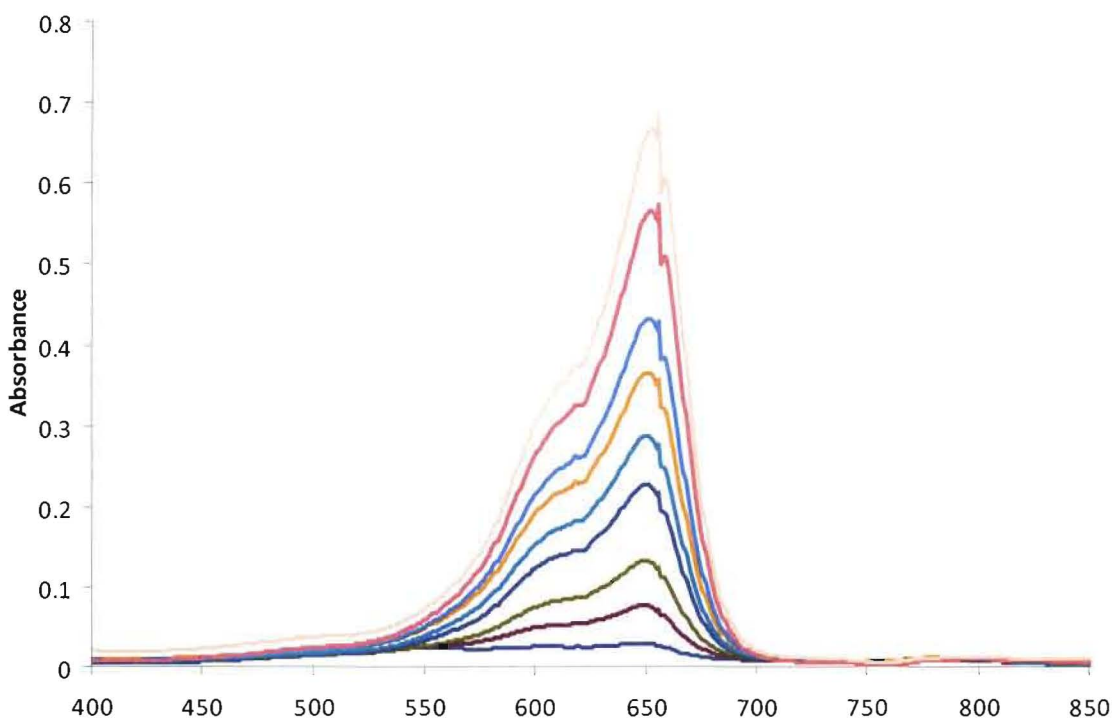


Figure 10. Optimal density gradient visualized by addition of methylene blue in chloroform.

4.3. Cyclohexane and Bromoform Density Gradient Centrifugation

Chloroform was replaced by a new solvent, bromoform, due to its high density of 2.89 g/mL. The idea was that the big difference in density between cyclohexane (0.779 g/mL) and bromoform (2.89 g/mL) would allow for a better size distribution throughout the tube because it

would be harder for these small particles to move through the more dense solution. A 10-step gradient was created in the same manner as described in the previous section for chloroform and cyclohexane. The tube was placed on its side for twenty minutes to allow the layers to begin to diffuse and 3 mL of the MoS₂ nanoparticles were carefully pipetted on top of the gradient. The solution was centrifuged for three minutes at 1000 rpm. Figure 11 shows the resulting solution.



Figure 11. Ultracentrifuge tube after centrifugation with cyclohexane/bromoform density gradient.

Nine fractions were harvested and fractions 2, 5, and 8 were analyzed using the transmission electron microscope. The TEM pictures are shown in Figures 12, 13, and 14 and show that there is a slight increase in size from fraction to fraction. However, there is only moderate size-fractionation using this method because, despite the slight increase in average size, there is still a polydisperse distribution of the particle sizes.

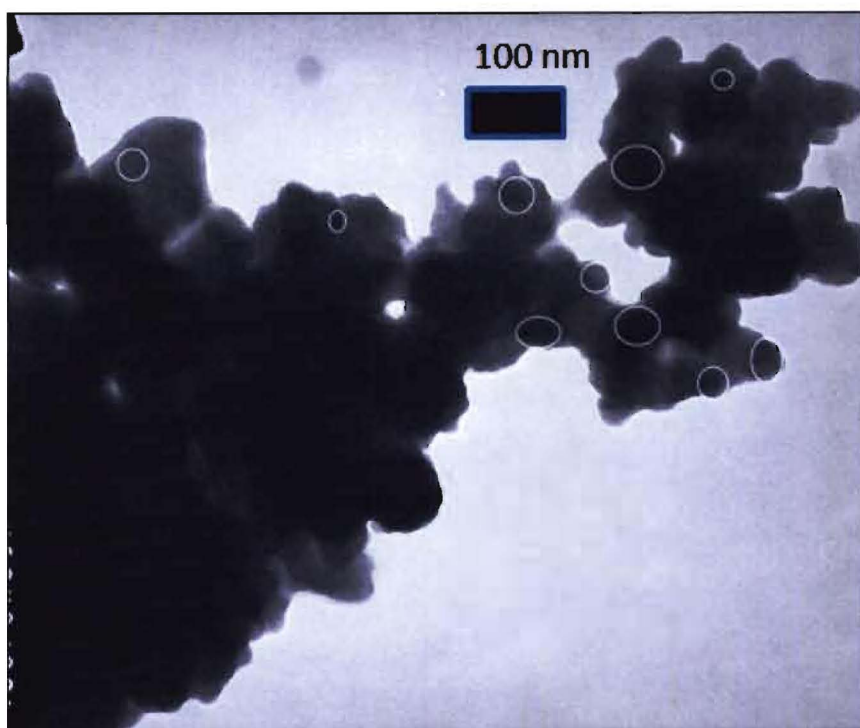


Figure 12. TEM image of fraction 2 using a cyclohexane/bromoform density gradient.

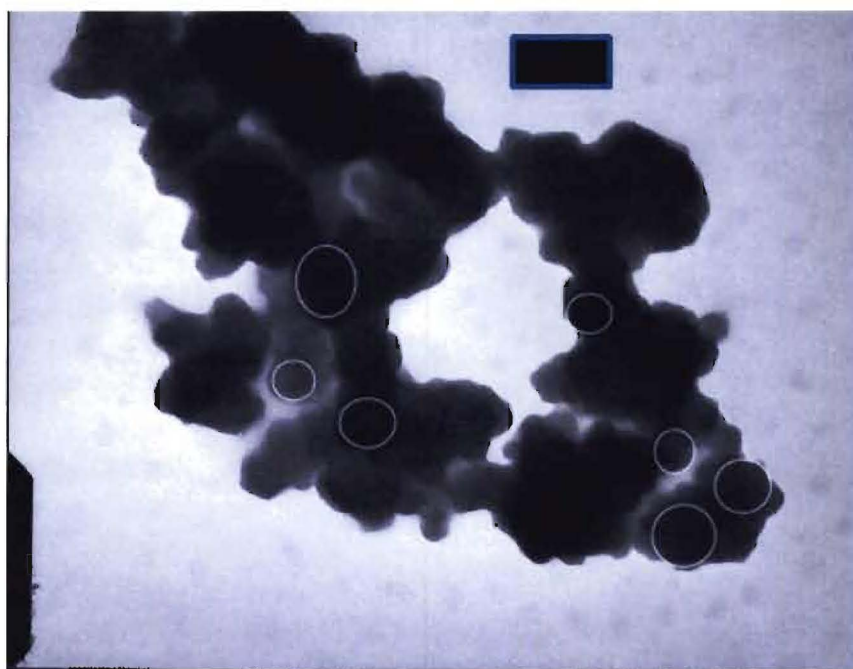


Figure 13. TEM image of fraction 5 using a cyclohexane/bromoform density gradient.

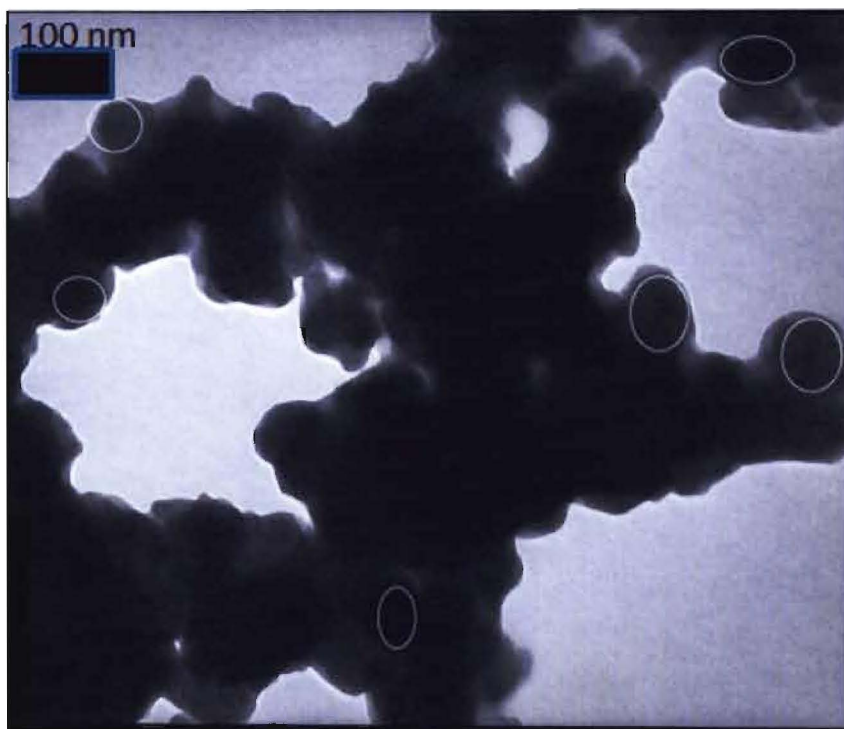


Figure 14. TEM image of fraction 8 using a cyclohexane/bromoform density gradient.

4.4. Density Gradient Centrifugation in Viscous Medium

The next ultracentrifugation method that was attempted used the same density gradient of cyclohexane and bromoform, but with the addition of a viscous medium.[6] The idea is to improve the separation by forcing the nanoparticles in between polymer chains in solution and to prevent the mixing of the separate fractions. Polystyrene was selected to create the viscous medium. The density gradient was created using the same 10-step gradient that was described previously. To add the polystyrene, 10 mL solutions of each of the 10-steps were made and 0.3 g of polystyrene was dissolved in each. 4 mL of each of the ten solutions were placed in the ultracentrifuge tube with increasing concentrations of cyclohexane. A 10% solution of cyclohexane was at the bottom and a 100% solution was at the top. 3 mL of the synthesized MoS₂ nanoparticles were carefully pipetted on top and the tube was centrifuged for seven minutes at 2,000 rpm. Figure 15 shows the ultracentrifuge tube after centrifugation.



Figure 15. Ultracentrifuge tube after centrifugation with cyclohexane/bromoform density gradient and a viscous medium.

Only three fractions were harvested because it appeared that there were three main zones in the centrifuge tube. Before the fractions could be analyzed, the polystyrene had to be removed. Each fraction was placed in an ultracentrifuge tube and washed four times with acetone by centrifuging it at 12,000 rpm for fifteen minutes; the supernatant was discarded after each wash.[8] The fractions were then dried in the vacuum dryer and re-dispersed in cyclohexane.

Transmission Electron Microscope images of the three fractions were taken and are shown in Figures 16, 17, and 18. There is slight size-fractionation between fractions one and three, but fraction two is not as clear. This is most likely due to the presence of polystyrene. A better method and more care must be placed into removing the polystyrene.

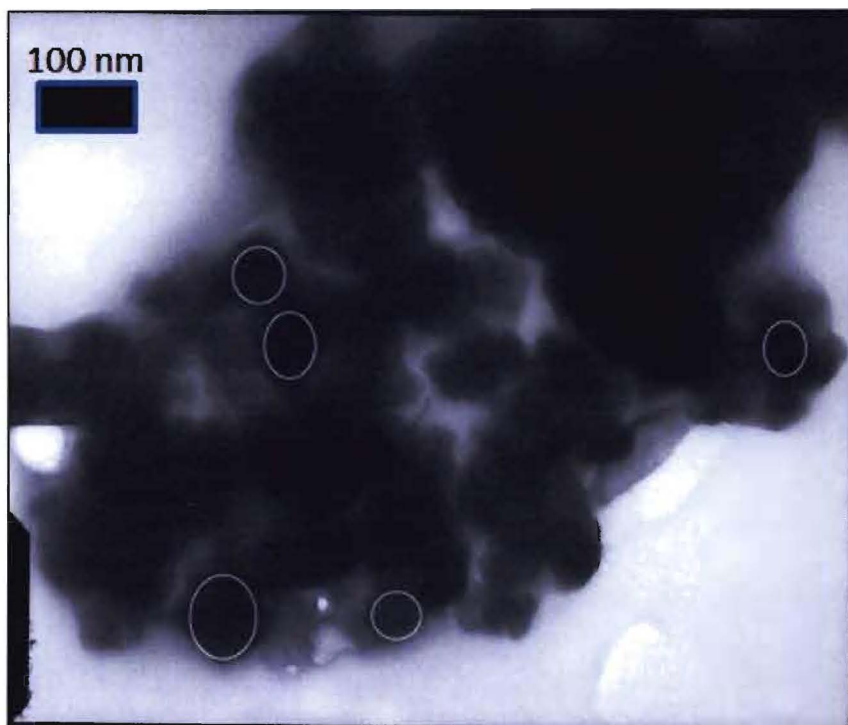


Figure 16. TEM image of fraction 1 using a cyclohexane/bromoform density gradient in a viscous medium.

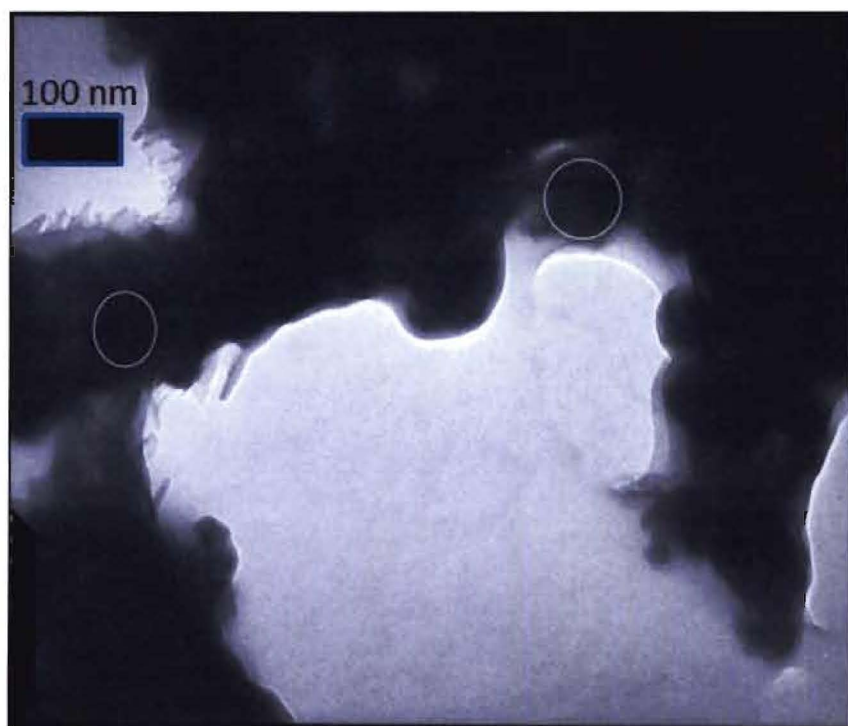


Figure 17. TEM image of fraction 2 using a cyclohexane/bromoform density gradient in a viscous medium.

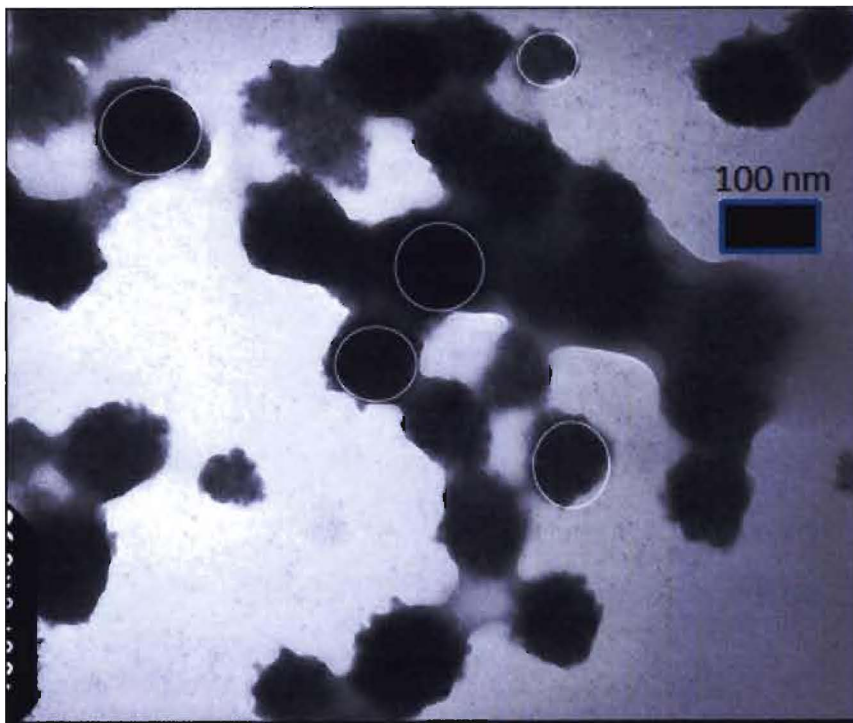


Figure 18. TEM image of fraction 3 using a cyclohexane/bromoform density gradient in a viscous medium.

Chapter 5. Solid Phase Extraction

Solid phase extraction is a separation process that is used to separate compounds according to their physical and chemical properties. In this method there are two main parts: the mobile phase and the stationary phase. The mobile phase is a sample suspended in liquid while the stationary phase is the solid medium that the sample will be passed through to separate the components due to differences in chemical affinities. In theory, because the synthesized MoS_2 nanoparticles have a very small size distribution and have many of the same properties on the nanometer scale they should elute at the same time. However, it is possible that the surfaces of different sizes have different properties that will react differently with the stationary phase and will elute at different times.

A highly-dispersed silica bed was used for the stationary phase and it was conditioned by rinsing with 3 mL acetone and 9 mL of cyclohexane. 2 mL of the synthesized nanoparticles were loaded into the column and a vacuum attachment was placed on top of the column. The sample was injected into the silica bed and then was washed with cyclohexane. Cyclohexane was consistently washed through the column for six hours at a flow rate of 1 mL every two minutes, but the line of particles present at the top of the silica bed did not move. The process was repeated again the next day with the same result. It is possible that despite being on the nanometer scale, the particles were still too large to be able to pass through the high-surface silica stationary phase.

Chapter 6. Size Exclusion Chromatography

Literature research revealed that there have been a few different studies that have used the method of size exclusion chromatography to separate particles based on size.[10,11,12, 13] The idea behind size exclusion chromatography is that samples are separated by virtue of their size in solution. Just as in solid phase extraction there is a mobile and a stationary phase. As a sample passes through the porous stationary phase large molecules cannot penetrate its pores as smaller ones can. As a result, large molecules spend less time in the column and elute faster than the small ones. The main use of this method is for large molecules and complexes such as proteins.[11] This posed a problem because those types of molecules are polar and water soluble while MoS₂ nanoparticles are very non-polar. The SEC columns used in the reports were meant for aqueous solvents. It first had to be determined if these columns would be able to handle the non-polar solvents that had to be used with MoS₂ nanoparticles.

The wetted materials in the aqueous columns are made of Teflon, polypropylene, borosilicate glass, and nitrile rubber. The effect of each of these materials to different non-polar solvents such as benzene, chloroform, cyclohexane, and toluene were researched to find the best fit. Benzene and toluene ended up being the most likely candidates. The wetted parts of a column were taken apart and placed in a beaker filled with benzene and toluene respectively and covered. They were left for three days to determine how they would react to the solvents and also to leech any unwanted material out of the parts. The plastic parts that were left in toluene swelled to the extent where they could not be put back together. This made that solvent useless. The parts fared much better in benzene, and the SEC column was able to be put back together. The column was then filled with benzene and left to sit for another two days to make sure none of the benzene would leak out of the column in some way. When checked there was the same amount of solvent. Benzene was selected as the solvent that would be used.

The stationary phase is a polystyrene that has a grain size of 200-400 μm . 12 grams of it was mixed with 50 mL of benzene and allowed to sit for 3 days for the pores to swell. The size exclusion column was filled with this mixture. A siphoning device was set up so that the column would be consistently filled to a certain point with benzene and so the stationary phase medium would not dry out. 2 mL of the synthesized MoS_2 nanoparticles were injected into the column. Benzene was continuously washed through the column to attempt to elute the particles. After four hours the particles had not moved past 1 cm so the benzene was run throughout the night. When checked in the morning the particles had not moved anymore. The column was cleaned out and the same procedure was run to confirm the result, and the particles did not migrate any further into the column.

One possibility for this is that the grain size was too small so none of the particles could move through the stationary phase. To try and solve this problem a coarser grain size was chosen. The new medium is a poly (styrene-co-divinylbenzene) polymer and has a mesh size of 300-500 μm . 24 g of this polymer was mixed with 100 mL of benzene and allowed to sit for three days for the pores to swell. The column was filled with the stationary phase and the same set-up as the previous size exclusion experiment was used. 2 mL of the MoS_2 nanoparticles were injected into the column. A possible difficulty that was observed was the color of the new stationary phase. The previous polystyrene medium that was used was a clear color which allowed for their location in the column to be observed. The new medium is a bright orange color and it is difficult to see where the line of brown-colored particles is. If the particles begin to separate in the column it will be hard to track their location and determine when some elute. Benzene began to be continuously run through the column to attempt to elute the particles. The experiment was run over night. The round bottom flask the benzene was eluting into was checked and no particles were present. Since the stationary phase was the bright orange color it could not be determined if the particles had moved at all and if they had where they were in the column. The experiment was run for another night but with the same result, none of the particles eluted out of the column.

Chapter 7. Conclusions

Molybdenum disulfide nanoparticles were synthesized in a simple one-pot set-up by decomposing Mo(CO)_6 in the presence of dissolved sulfur. The particles obtained were in the 5-40 nm size range and they were used in the different size-fractionation techniques. From experimenting with the different techniques a few conclusions can be made:

1. Simple sedimentation ultracentrifugation in pure cyclohexane allowed for moderate size fractionation, but it was not a very efficient method because there was still a polydisperse distribution of sizes in each fraction.
2. Density gradient centrifugation using bromoform and cyclohexane as the solvents also led to moderate size fractionation.
3. Density gradient centrifugation with a viscous medium allowed for slight size-fractionation between fractions one and three, but was inconclusive due to the presence of polystyrene. A better method and more care had to be placed into removing the polystyrene for this method to be attempted.
4. Solid phase extraction with a highly-dispersed silica bed for the stationary phase and the MoS₂ nanoparticles dispersed in cyclohexane as the mobile phase allowed for no separation. Despite being on the nanometer scale, the particles were still too large to be able to pass through the high-surface silica stationary phase.
5. Size-exclusion chromatography using two different grain sizes (200-400 and 300-800µm) posed the same problem as solid phase extraction. The particles could not make it through the column to elute.

Out of all the size-fractionation techniques attempted the most effective were sedimentation centrifugation and simple density gradient centrifugation without the viscous medium. However, those only yielded crude fractionation because there was still a polydisperse distribution of sizes.

References

1. Wilcoxon, J. P. J. Phys. Chem. B 2000, 104, 7334-7343.
2. Kelley, David F. "Spectroscopy and Dynamics of Layered Semiconductor Nanoparticles" *Semiconductor Photochemistry and Photophysics*. **2003**, 10, 167-199.
3. Thurston, T.R.; Wilcoxon J.P. J. Phys. Chem. B 1999, 103, 11-17.
4. Wilcoxon, J. P.; Samara, G. A. Phys. Rev. B 1995, 51, 7299-7302.
5. Duphil, D. et al. Nanotechnology 2004, 15, 828-832.
6. Bai, L. et al. J. Am. Chem. Soc. 2010, 132, 2333-2337.
7. Sun, X. et al. Angew. Chem. Int. Ed. 2008, 47, 1-5.
8. Siporska, A.; Szydłowski, J. J. Polymer Science. 2009, 47, 2140-2143.
9. Howard, A. J. Environ. Monit. 2010, 12, 135-142.
10. Wilcoxon, J.P.; Martin, J.E.; Provencio, P. Langmuir 2000, 16, 9912-9920.
11. Krueger, K.M.; Al-Somali, A.M.; Falkner, J.C.; Colvin, V.L. Anal. Chem. 2005, 77, 3511-3515.
12. Novak, J.P.; Nickerson, C.; Franzen, S.; Feldheim, D.L. Anal. Chem. 2001, 73, 5758-5761.